

## PATENT SPECIFICATION

(11) 1291 387

NO DRAWINGS

**1 291 387**

(21) Application No. 7500/70 (22) Filed 17 Feb. 1970  
 (31) Convention Application No. 2401 (32) Filed 21 Feb. 1969 in  
 (33) Sweden (SW)  
 (45) Complete Specification published 4 Oct. 1972  
 (51) International Classification C23C 11/08  
 (52) Index at acceptance

C7F 1B2 2M 2Z2 2Z5 4E 4F 4K



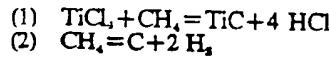
**(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF  
A COATED SINTERED HARD METAL BODY**

(71) We, SANDVIKENS JERNVERKS AKTIEBOLAG, a Swedish Body Corporate of Sandviken, Sweden, do hereby declare the invention, for which we pray that a patent 5 may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a method of coating a sintered hard metal body consisting of metallic carbide bound with a binder metal with a carbide layer formed on the said body by deposition from a gas. The present invention is related to the invention disclosed in our co-pending Application No. 7615/70 (Serial No. 1,291,388) claiming the same priority date of the 21st February 1969. With the present invention it is possible to provide the sintered hard 15 metal body with a thin, extremely hard and wear-resistant carbide layer.

It is known that surface layers consisting of carbides of one or some of the elements belonging to the 3rd up to and including 25 the 6th groups of the Periodic System can be applied to metallic and other materials. Such layers, for instance consisting of TiC, may be applied to a metallic support or substratum by deposition at an elevated temperature from a gaseous phase containing 30 metal halide, hydrocarbon and hydrogen.

The above-mentioned process may for instance comprise titanium tetrachloride, methane and hydrogen, and *inter alia* the following reactions are important:



In order to avoid a precipitation of free carbon together with the carbides it is customary to use gas mixtures, which do not contain a greater part of volatile hydrocarbon compounds than corresponds to the equilibrium of the reaction (2) at the precipitation temperature, and in which not 40 more, but preferably as much metal halide 45

is included, as is equivalent with the volatile hydrocarbons (reaction 1).

The reactions, which occur in the formation of carbide layers on hard metals as substrata, have however not earlier been closely investigated and it has probably been assumed schematically that the process in general ought to follow the mentioned type-reaction, comprising gaseous metal halide and hydrogen and also hydrocarbon, for instance methane, as a carbon-providing medium. The possibility of producing a carbide layer by reactions at which the hard metal substratum itself has been able to supply the necessary amount of carbon during the process has been considered seriously.

The reason for this opinion was the experience obtained from coating of steel, showing that steels containing elements which are normally included in hard metal like W, V, Mo and others, and which at the same time had a high carbon content, were not able to provide carbon for forming, for instance, surface-coatings of TiC, because the carbon was firmly bound in the form of carbides with the mentioned elements of the steel.

In practical use of carbide-coated hard metal bodies for instance in the field of chip cutting machining, there have up to now been obtained very unreliable results, which has been a serious disadvantage.

Surprisingly it has now been found, that under certain circumstances it is possible to produce a carbide surface layer with excellent properties in several respects on a hard metal substratum.

According to this invention we provide a method of coating a sintered hard metal body comprising metallic carbide bound with a binder metal the method comprising coating the said body (A) with a carbide layer (B) chosen from titanium carbide, niobium carbide, tantalum carbide, zirconium carbide, hafnium carbide, vanadium carbide and tungsten carbide, the said layer (B) being formed on the said body (A) by conducting

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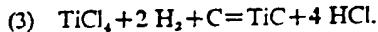
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a gas at elevated temperature over the body (A), the said gas containing (i) one or more gaseous metal compounds corresponding to the composition of the carbide layer (B) required and (ii) a content of carbon which is less than the amount required for carbide formation. The said body (A) contains one or more of WC, MoC, CrC and optionally one or more of TiC, TaC, NbC, VC, ZrC, HfC bound with one or more of Co, Ni, Fe, Cr. The said body (A) may also contain one or more of the borides, silicides and/or nitrides of the metals W, Ti, Ta, Nb, Mo, Cr, V, Zr, Hf, Co, Ni, Fe. Preferably the said content of carbon (ii) is provided by hydrocarbon, and preferably some of the carbon required for the formation of the carbide layer (B) is derived from the surface of the carbide body (A). Expediently, the said gas used in the method of this invention has a composition such that at most 40 percent, preferably at most 20 percent, of the carbon required for the formation of the carbide layer (B) is derived from the said gas. This means that the body (A) will have to contribute nearly all of the carbon which is necessary for the carbide formation. In this case the reaction can for instance be illustrated by the chemical equation:



It has thus been possible to adapt and change the deposition process mentioned before, which in itself is well-known, so that the chemical transformation mainly proceeds according to the reaction (3), although this from a thermo-dynamic point of view may seem less favourable than the reaction (1). That has been made possible, for instance by using suitably adjusted amounts of hydrogen and metal halide whilst maintaining the before-mentioned carbon deficit in the gaseous phase. Thus, it is preferred that the said gas should comprise metal halide, hydrogen and hydrocarbon. An addition of gaseous hydrocarbon to the metal halide hydrogen gas mixture entering reaction vessel should generally be entirely avoided. The hydrocarbon should not generally exceed 1% by volume and preferably not exceed 0.5% by volume of the said gas. Under the circumstances, under which the reaction normally occurs, i.e. a temperature between 700—1100°C and a gas pressure between 1—100 mm Hg, the volume of metal halide may be 0.01—0.04 of the volume of hydrogen, preferably more than 0.02 and less than 0.03 of the volume of hydrogen. The reaction time, the exact length of which is determined by the above-mentioned process-variables, is normally 1—6 hours de-

pending *inter alia* on the desired thickness of the layer. In general a reaction time is used, which exceeds 2 hours and preferably at the most lasts up to 5 hours.

Although the carbon in the hard metal substratum is very firmly bound in form of carbides of metals e.g. the carbides of W, Ta, Nb, Ti and others, it is possible to regulate the process so that a thin intermediate layer of the hard metal is decarburized. This carbon diffuses to the surface and reacts with for instance the metal halide in question and hydrogen, forming the carbide layer. It has been found very important for obtaining more uniform and better results in practical use that the above-mentioned decarburized intermediate layer should have a definite composition and extent.

This has been made possible by the before-mentioned determining of the process variables, also by determining the conditions of the composition, which the hard metal support of the substratum has to fulfil.

Hard substances, which have been found to be suitably active to act as carbon providers, that is carbides of W, Mo and/or Cr, must be included, preferably at contents of at least 10% by volume, more preferably over 35% by volume, WC preferably being included as a component.

The binder metal consists normally of Co, Ni and/or Fe, preferably Co, and may be included in the body (A) in contents of between 2—30% by volume, preferably more than 5% and at most 25% by volume, for instance between 15—20% by volume.

Other hard substances, which have been found generally to be too stable to give up carbon to any appreciable degree, as for instance carbides of Ti, Zr, Hf, Ta, Nb, and V, i.e. mainly carbides with so-called cubic crystal structure, may constitute the remainder.

The composition of the above-mentioned intermediate layer will generally correspond to certain low carbon phases in the three component system W—Co—C, in the first place so called eta-phase, usually written Co<sub>3</sub>W<sub>2</sub>C, an in itself well-known structural constituent in the cemented carbide field. It has often been found advantageous to substitute for Co in the mentioned phases entirely or partly Fe, Ni, and/or Cr.

A noticeable decarburization occurs to a depth of in general at least 20 µm beneath the surface of the body (A), while the distinctly marked relatively uniformly developed intermediate layer, which consists essentially of low carbon phases, has a thickness of the order of 1—12 µm. Preferably the thickness of the intermediate layer should, however, exceed 3 µm and in most cases be below 10 µm.

Among the factors which contribute to the improved properties of the coated body pro-

duced according to the invention, may be pointed out the levelling of unfavourable differences in quality inside the substratum or body (A) and between the substratum or body (A) and carbide layer (B) for instance with regard to thermal expansion and mechanical strength.

A further advantage is the exceptionally good bond between body (A) and layer (B) (of so called metallurgical type) which is the result when the before-mentioned low carbon phases are formed and grow simultaneously with a titanium carbide layer (B) on hard metal (A).

Another noteworthy advantage is the remarkable increase of hardness, due to the decarburization in the substratum or body (A) immediately below the carbide surface layer, indicating for instance increased resistance to plastic deformation of the coated hard metal body.

The precipitated surface layer (B), which should desirably be very thin, generally between 1—12  $\mu\text{m}$  and often about 2—6  $\mu\text{m}$  consists of extremely fine grained carbide, for instance TiC, NbC, and/or TaC.

It has been found very advantageous, if the carbide layer (B) is so composed that it is double-layered and consists of a particularly fine-grained inner layer next to the body (A) and a somewhat more coarse grained growth region constituting an outer layer at the surface of layer (B). The mean grain size of the said inner layer should desirably be 0.02—0.15  $\mu\text{m}$  and that of the growth region 0.2—0.4  $\mu\text{m}$ . As an example there may be mentioned a mean grain size of the inner layer of about 0.1  $\mu\text{m}$  and that of the growth region of about 0.3  $\mu\text{m}$ .

Coated bodies manufactured according to the invention are especially characterized in a very good and uniform quality in practical use. Among the reasons for this may be mentioned the improved adherence between layer (B) and body (A), the increased resistance against *inter alia* thermoshocks and mechanical impact stresses, and improved resistance of the body (A) against plastic deformation.

Among the fields of application, where coated hard metal produced according to the invention has shown superior qualities compared to conventional hard metal may be mentioned tools and inserts for chip cutting machining, inserts and wear parts in rock drilling, cold- and hot-forming tools including tools for wire, strip or tube drawing, shearing and pressing tools, sealing means for pumps and similar and wear parts of different kinds.

In a wider sense the quality improving effect, which a carbide coating has upon a hard metal body is based on metallurgical laws of partly complex nature. In certain fields of use, for example chip forming mach-

ining, the favourable effect which may be obtained by an addition of TiC to normal hard metal of WC-Co-type is well known. TiC and other carbides contribute to a decreased speed of the diffusion-natured, wear-causing reactions between hard metal insert and work piece during the cutting operation.

An advantage of the product of the invention is that for instance a TiC layer deposited on the hard metal body serves as a so-called diffusion barrier, which prevents harmful wear reactions. At the same time the hard metal body maintains its original excellent strength properties.

The following Example 1 illustrates the conditions under which sintered hard metal bodies (A) have been coated with a layer (B) of TiC in accordance with an embodiment of the invention.

#### Example 1

Coating took place in a retort, i.e. a reaction vessel of a type known in itself, permitting evacuation, throughflow of gas and heating up to high temperature.

*Body (A):* 1000 pieces of precision-ground hard metal inserts, intended for cutting. Hard metal grade containing 40% by volume WC, 15% by volume Co and 45% by volume cubic carbides in form of TiC, TaC and NbC.

*Coating:* The hard metal inserts were placed in the retort, whereupon a gas with the composition (in % by volume): 97 H<sub>2</sub>, 2.5 TiCl<sub>4</sub>, 0.5 CH<sub>4</sub>, was passed through the charge. The gas pressure was 20 mm Hg and the incoming gas flow 760 Ncm<sup>3</sup>/min. The reaction took place at 875°C and the coating obtained the desired thickness after 2.5 hours to provide layer (B).

*Result of the coating:* The metallographic and physical examinations showed that the surface layer of TiC was uniformly developed with a compact, pore free structure and a thickness of about 4  $\mu\text{m}$ . Nearest the body (A) was observed an inner more fine grained region with a grain size of about 0.09  $\mu\text{m}$ . The outer region had a grain size of about 0.3  $\mu\text{m}$ .

The intermediate layer bordering on the TiC-layer on the body (A) showed a uniformly decarburized zone with a thickness of about 7  $\mu\text{m}$ . W-Co-C-phases that were present consisted mainly of eta-phase, but also some other phases were observed.

The following Example 2 shows the great improvements, which can be obtained by the product of the invention. Comparison has here been made in the field of cutting between inserts coated with a TiC-layer according to the invention, inserts coated with a layer according to a prior method where the necessary amount of carbon for the carbide formation is added mainly by means of gaseous hydrocarbon, and known uncoated inserts.

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Example 2  
Turning of carbon steel having a C-content of 1% by weight. Tool wear after a predetermined cutting time at given constant cutting conditions.

Flank wear respectively cratering

	Hard metal grade	Flank wear	Crater depth	Time
5	(1) (with layer (B) produced according to the invention)	0.09 mm	<5 $\mu\text{m}$	15 min.
	(2)	0.20 mm	56 $\mu\text{m}$	15 min.
	(3)	0.10 mm	7 $\mu\text{m}$	15 min.
10	(1) (uncoated)	0.97 mm	318 $\mu\text{m}$	15 min.
	(1) (with non-uniform layer)	0.80 mm	283 $\mu\text{m}$	15 min.

	In several different operations demanding high toughness the coated (1) inserts showed the same strength as the corresponding uncoated inserts and corresponding inserts of grade (1) coated with a non-uniform layer.	Cutting data (continued)	20
15	Cutting data	Cutting depth: 2.0 mm. Entering angle: 75°. Material: Carbon steel, make "Sandvik" 17C (1% by weight C).	
	Cutting speed: 120 m/min. Feed: 0.30 mm/rev.		25

Composition in % by weight of the hard metal:									
Grade	Co	Ni	Mo	TiC	TaC	NbC	Cr <sub>3</sub> C <sub>2</sub>	WC	
30	(1)	9.5	—	—	11.9	6	4	—	rest
	(2)	9.5	—	—	19	12.2	3.8	—	rest
	(3)	—	10	2	60	3	2	5	rest

From this Example it is thus clear that the resistance of flank wear has in broad outline increased 10 times by applying the improved carbide surface layer, and that an enormous increase of the cratering resistance has taken place.

It can further be stated that inserts of grade (1), with maintained toughness, coated according to the invention, have reached the same wear-resistance as corresponding tools in the extremely wear-resistant but at the same time considerably less tenacious grade (3).

**WHAT WE CLAIM IS:—**

45. 1. A method of coating a sintered hard metal body (A) containing one or more of WC, MoC, CrC and optionally one or more of TiC, TaC, NbC, VC, ZrC, HfC bound with one or more of Co, Ni, Fe, Cr, the method comprising coating the said body (A) with a carbide layer (B) chosen from titanium carbide, niobium carbide, tantalum carbide, zirconium carbide, hafnium carbide, vanadium carbide and tungsten carbide, the said layer (B) being formed on the said body (A) by conducting a gas at elevated temperature over the body (A), the said gas containing (i) one or more gaseous metal compounds corresponding to the composi-
50. tion of the carbide layer (B) required and (ii) a content of carbon which is less than the amount required for carbide formation.
55. 2. Method according to Claim 1, wherein in the said body (A) also contains one or more of the borides, silicides and/or nitrides of the metals W, Ti, Ta, Nb, Mo, Cr, V, Zr, Hf, Co, Ni, Fe.
60. 3. Method according to Claim 1 or Claim 2, wherein the said content of carbon (ii) is provided by hydrocarbon.
65. 4. Method according to any preceding claim, wherein some of the carbon required for the formation of the carbide layer (B) is derived from the surface of the carbide body (A).
70. 5. Method according to any preceding claim, wherein the said gas has a composition such that at most 40 percent of the carbon required for formation of the carbide layer (B) is derived from the said gas.
75. 6. Method according to Claim 5, wherein the said gas has a composition such that at most 20 percent of the carbon required for formation of the carbide layer (B) is derived from the said gas.
80. 7. Method according to any preceding Claim, wherein the said gas comprises metal halide, hydrogen and hydrocarbon.
85. 8. Method according to Claim 7, where-

in the said gas contains no more than one percent by volume of hydrocarbon.

9. Method according to Claim 8, wherein the said gas contains no more than 0.5 percent by volume of hydrocarbon.

10. Method according to any one of Claims 7 to 9, wherein the amount by volume of metal halide in the said gas is 0.01 to 0.04 of the amount by volume of hydrogen in the said gas.

11. Method according to Claim 1 substantially as herein described and exemplified.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1972.  
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY  
from which copies may be obtained.